PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-228873

(43)Date of publication of application : 24.08.1999

(51)Int.Cl. C09D 7/00

(21)Application number : 10-051556

(22)Date of filing : 16.02.1998

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(54) TITANIUM DIOXIDE PHOTOCATALYST-CONTAINING COATING MATERIAL COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition having functions such as deodorizing, atmosphere cleaning, self-cleaning and antimicrobial properties by dispersing a porous silica-coated titanium dioxide photocatalyst and a pigment titanium dioxide in a vehicle so as to provide the contents thereof in a dried coating film with respective specific ranges.

SOLUTION: This composition is obtained by dispersing preferably 30-60 wt.% of preferably an anatase type porous silica-coated titanium dioxide photocatalyst and preferably 5-20 wt.% of preferably a rutile type pigment titanium dioxide in an organic resin coating material vehicle so as to respectively provide 5-70 wt.%, preferably 30-60 wt.% content of the anatase type porous silica-coated titanium dioxide photocatalyst in a dried coating film and 5-60 wt.%, preferably 5-20 wt.% content of the rutile type pigment titanium dioxide in the dried coating film. Thereby, the deterioration of the organic vehicle resin by the photocatalyst can be suppressed.

LEGAL STATUS

[Date of request for examination] 02.02.2005

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001] Field this invention of this invention relates to the titanium-dioxide photocatalyst content coating constituent which has functions, such as deordorization, atmospheric-air purification, self-cleaning, and antibacterial.
[0002] The photocatalyst activity of a particle titanium dioxide is used in recent years [background technical], photochemical reaction decomposes harmful matter and research which is going to remove thru/or defang is done briskly. Since the titanium dioxide used as a photocatalyst is generally a particle thru/or an ultrafine particle with a mean particle diameter of 0.1 micrometers or less, it must fix a photocatalyst to a base material in a certain form in order to avoid scattering and an outflow. It is the approach of forming the paint film which distributes and coating-izes the one fixed approach in the inorganic binder which cannot receive photodegradation easily, for example, a silica sol, applies this to a base material, dries, and contains a photocatalyst (JP,8-164334,A).
[0003] When an inorganic binder is used, it is less than the coating which uses organic resin as a binder in the paint film engine performance, especially shock resistance that the binder itself deteriorates with a photocatalyst, although avoided.
[0004] In order to control degradation by the photocatalyst of the paint film which used the organic resin binder, porosity microencapsulation of the mixture of a titanium-dioxide photocatalyst and an inorganic system deordorization adsorbent is carried out using a silica sol, and the approach of distributing this to organic resin is indicated by JP,9-31335,A. However, in order to make below into a fixed grain size the particle which grew up to be an aggregated particle by condensation in order to distribute a pigment in coatings generally at homogeneity, it must grind mechanically in a binder using a mill. If a part of porosity inorganic enveloping layer [at least] of a photocatalyst is destroyed by the physical stress at this time and it comes to contact binder resin and directly, chalking-ization of the paint film by the photodegradation of resin will be promoted. The same problem is encountered even if it uses the photocatalyst which coated the front face with the porosity silica.
[0005] The indication of this invention, then this invention offer the coating constituent containing a porosity silica covering titanium-dioxide photocatalyst in which binder resin does not deteriorate according to a photocatalyst operation comparatively for a long period of time, maintaining desired catalytic activity level also according to the distributed process which is not avoided on the occasion of coating-izing.
[0006] As for this invention, the inside of a dry paint film and a porosity silica covering titanium-dioxide photocatalyst content offer the titanium-dioxide photocatalyst content coating constituent which distributes a porosity silica covering titanium-dioxide photocatalyst and a pigment titanium dioxide in an organic resin vehicle, and becomes so that 5 - 70 % of the weight (preferably 30 - 60 % of the weight) and a pigment titanium-dioxide content may become 5 - 50 % of the weight (preferably 5 - 20 % of the weight).
[0007] Since it must have a large specific surface area in order to function as a detailed argument photocatalyst, the particle thru/or ultrafine particle of several nm thru/or several 10nm range is used. On the other hand, the pigment titanium dioxide usually has the particle size of 0.2-0.3 micrometers (200-300nm). Although a pigment titanium dioxide is widely used as large white pigments of obliterating power by difference of such particle diameter, a particle titanium dioxide does not have such optical property. moreover, a pigment titanium dioxide -- a front face -- ZnO, aluminum 2O3, SiO2, TiO2, and ZrO2 etc. -- photocatalyst activity is controlled by coating with water oxide. Coating by a silica etc. is performed so that the particle titanium dioxide used as a photocatalyst may not contact matric resin and directly, either. However, since it must have the front face which contacts the open air in this case, there are also few amounts of coatings as compared with a pigment titanium dioxide, and an enveloping layer is porosity.
[0008] Such a titanium-dioxide photocatalyst by which porosity covering processing was carried out is marketed as photocatalyst titanium oxide STE series from Ishihara Sangyo Kaisha, Ltd. The crystal form of the titanium dioxide used as a photocatalyst is usually an anatase mold.
[0009] As for the pigment titanium dioxide, the thing of various brands is marketed by the application from each company. Generally the rutile mold excellent in weatherability is used for coatings, and this is desirable also in this

invention.
[0010] As discussed until now, generally the catalytic activity and chalking-proof nature of a titanium-dioxide photocatalyst paint film which were fixed with organic matrix resin are incompatible. If it puts in another way, the paint film which has high catalytic activity will tend to start a chalking for a short period of time. this invention persons discovered that a chalking-proof life was extensible for useful purpose by using together a titanium-dioxide photocatalyst and a pigment titanium dioxide at a fixed rate, maintaining catalytic activity on request level.
[0011] Consequently, the pigment weight concentration PWC of the photocatalyst in a dry paint film found preferably that 5 - 20% was suitable 5 to 50% for PWC of a pigment titanium dioxide 30 to 60% 5 to 70%. Total PWC is preferably [40 - 70% of] suitable at least 40%.
[0012] Organic resin constitutes the matrix of a photocatalyst and a pigment titanium dioxide out of a dry paint film. Although the organic resin used is easy to be the thing of common use, fluorine-containing ****** acrylic silicone system organic resin is especially desirable. Probably these components are common knowledge in the field of a coating, and the detailed explanation beyond this will be unnecessary.
[0013] Coating-ization adds other additives to the varnish of binder resin according to a photocatalyst, a pigment titanium dioxide, and the need, and it distributes them to homogeneity until it reaches request grain size using the various mills for coatings, as stated previously. The mill which uses dispersion-medium objects, such as a glass bead, is desirable.
[0014] Paint can be carried out using general painting methods, such as a brush, a roller, and spraying. Although base materials are a metal, glass, the ceramics, concrete, wood, etc., after they perform blasting processing and primer spreading in order to raise adhesion, they may be painted.
[0015] By disassembling the harmful matter in atmospheric air by the photochemical reaction by the titanium-dioxide photocatalyst, in spite of the formed paint film demonstrating functions, such as deordorization, atmospheric-air purification, self-cleaning, and antibacterial, and using organic resin for it, its service life is long.
[0016] In the following examples, it is based on weight criteria the "section" and"%."
[0017] Dispersion-liquid No.1-No.8 of the combination shown in example 1 table 1 were prepared.
[0018]
[Table 1]
表 1

原料（重量部）	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8
ＳＴＥ－０１ [1]	50	30.5	27.8	25.05	19.6	14.15	8.7	0
アクリディックA-801 [2]	48	48	48	48	48	48	48	48
酢酸ブチル	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5
DISPERBYK 163 [3]	3	3	3	3	3	3	3	3
タイペークCR-97 [4]	0	0	2.7	5.45	10.9	16.35	21.8	30.5
計	119.5	100	100	100	100	100	100	100

1）石原産業（株）製多孔質シリカ被覆二酸化チタン光触媒
2）大日本インキ化学工業（株）製アクリルポリオール
3）ＢＹＫ社製顔料分散剤
4）石原産業（株）製ルチル型二酸化チタン顔料

[0019] Raw material mixture was put into the beaker, the glass bead (Toshiba) 300 weight section with a particle size of 1.2-1.5mm was supplied to this, the dissolver distributed for about 20 minutes at the rate of 1200rpm, the glass bead after distributed termination was filtered and removed, and dispersion liquid were obtained.
[0020] this dispersion-liquid 90 weight section and Sumitomo Bayer Urethane -- the make HDI system poly isocyanate curing agent N-75 (60% butyl-acetate solution) 10 weight section and the butyl-acetate 45 section were mixed, and it considered as coating liquid.
[0021] Spray painting of this coating liquid was carried out to the glass plate and the plate painted [fluorine enamel], respectively, it dried for 14 days at the room temperature, and the color card was obtained.
[0022] It is JIS which was applied to the plate painted [fluorine enamel]. The sunshine weather meter specified to K5400 performs the accelerated exposure test of 1000 hours, and it is JIS about whenever [paint film degradation]. Whenever [chalking / which is specified to K5400] estimated.

[0023] The color card applied to the glass plate is on-the-strength 5 mW/cm2. After irradiating the black light with a dose for 48 hours, the following test methods estimated NO gas resolvability ability.
[0024] NO gas resolvability ability test-method testing device: The black light which maintained spacing of 5mm with a quartz-glass plate at the box made of acrylic resin which covered the top face which has a gas inlet and an outlet with the quartz-glass plate, fixed to it, and installed the 50x300mm test piece above quartz glass in it to exposure energy 1.5 mV/cm2 Ultraviolet rays are irradiated at a test piece.
Test method: Pass said equipment for 60 minutes and make it equilibrate air with a NO gas concentration of 3 ppm by the flow rate of 1.5 L/min before measurement initiation. the inlet port and outlet of equipment after reaching a balance -- setting -- each NO concentration in gas -- NOIN and NOOUT It measures and NO gas cracking severity (%) is searched for using the following formulas.
Cracking-severity (%) =(NOIN-NOOUT) x100/NOIN result: The effect to whenever [photocatalyst / in a paint film / and chalking / of a pigment titanium-dioxide content], and NO cracking severity is shown in Table 2.
[0025]
[Table 2]
表 2

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
総PWC (%)	61.9	50.7	50.7	50.7	50.7	50.7	50.7	50.7
光触媒PWC (%)	61.9	50.7	46.2	41.7	32.6	23.5	14.5	0.0
顔料TiO$_2$ PWC (%)	0.0	0.0	4.5	9.1	18.1	27.2	36.3	50.7
白亜化度	0	0	6	8	8	8	8	8
塗膜外観*	×	×	○	○	○	○	○	○
NO分解率 (%)	81.8	82.6	78.1	73.4	55	24.8	5.3	0

注) ○：変化なし　　×：塗膜崩壊

[0026]
Example 2 Fluororesin coating (isocyanate bridge formation form)
Resin : Lumiflon LF-100 The 48.0 sections Photocatalyst : [TIPAQUE STE-01] The 27.8 sections Color pigment : [TIPAQUE CR-97] The 2.7 sections Solvent : [Butyl acetate] The 18.5 sections Lumiflon LF-100 : The raw material mixture of the fluorine resin system polyol above by Asahi Glass Co., Ltd. is put into a beaker. The glass bead 200 weight section with a particle size of 1.2-1.5mm was supplied to this, the dissolver distributed for about 20 minutes at the rate of 1200rpm, filtration removed the glass bead after distributed termination, and dispersion liquid were obtained. This dispersion-liquid 90 section, the curing agent (N-75 60% butyl-acetate solution of poly isocyanate curing agents made from Sumitomo Bayer Urethane) 10 weight section, and the butyl-acetate 45 section were mixed, and it considered as coating liquid.
[0027]
Example 3 Fluororesin coating (melamine bridge formation form)
Resin : Lumiflon LF-100 The 48.0 sections Photocatalyst : [TIPAQUE STE-01] The 25.05 sections Color pigment : [TIPAQUE CR-97] The 5.45 sections Solvent : [Butyl acetate] The 18.5 sections Additive: DISPER BYK163 The raw material mixture of the 3.0 section above was put into the beaker, the glass bead 200 weight section with a particle size of 1.2-1.5mm was supplied to this, the dissolver distributed for about 20 minutes at the rate of 1200rpm, filtration removed the glass bead after distributed termination, and dispersion liquid were obtained. This dispersion-liquid 90 section and melamine resin 325 made from Mitsui SAINAMIDDO Ten weight sections and the butyl-acetate 45 section were mixed, and it considered as coating liquid.
[0028]
Example 4 Acrylic silicone coating Resin : [ZEMURAKKU AM 1532] The 48.0 sections Photocatalyst : [TIPAQUE STE-01] The 25.05 sections Color pigment : [TIPAQUE CR-97] The 5.45 sections Solvent : [Butyl acetate] The 18.5 sections ZEMURAKKU AM 1532 : The Kaneka Co., Ltd. make The raw material mixture of the acrylic silicone resin above was put into the beaker, the glass bead 200 weight section with a particle size of 1.2-1.5mm was supplied to this, the dissolver distributed for about 20 minutes at the rate of 1200rpm, filtration removed the glass bead after distributed termination, and dispersion liquid were obtained. This dispersion-liquid 100 section, the xylene solution (dibutyl tin JIRAU rate: xylene =1:9) 1 section of a dibutyl tin JIRAU rate, and the butyl-acetate 45 section were mixed, and it considered as coating liquid.
[0029]

Example 5 Fluorine emulsion plastic paint ZEFFLE SE-310 1 The 48.0 sections TEKISA Norian 2 The 4.8 sections TIPAQUE STE-01 The 25.05 sections Day spa tick SMA 3 The 1.0 sections Ply mull RM-8 (25% propylene glycol solution) 4 The 0.3 sections Deionized water The 9.95 sections The NOPUKO 8034 5 1.0 section RIOFASUTO H-201 6 The rutile mold diacid-ized titanium pigment part water spray nature paste above-mentioned raw material mixture is put into a beaker. two by 9.9 section 1 Daikin Industries, LTD. -- 4 made from Eastman Chemical 3 Japanese Flower Chemistry loam, and 6 TOYO INK MFG. CO., LTD. make by 5 Sannopuko made from HASU -- The dissolver distributed for about 20 minutes at the rate of 1200rpm, this dispersion-liquid 100 section and the deionized water 20 section were mixed, and it considered as coating liquid.

[0030]

Example 6 Acrylic polyol plastic paint (isocyanate bridge formation form)

Resin : AKURIDIKKU A-801 The 48.0 sections Photocatalyst : [TIPAQUE STE-01] The 25.05 sections Color pigment : [TIPAQUE CR-97] The 5.45 sections Solvent : [Butyl acetate] The 18.5 sections Additive: DISPER BYK163 The raw material mixture of the 3.0 section above was put into the beaker, the glass bead 200 weight section with a particle size of 1.2-1.5mm was supplied to this, the dissolver distributed for about 20 minutes at the rate of 1200rpm, filtration removed the glass bead after distributed termination, and dispersion liquid were obtained. This dispersion-liquid 90 section, the curing agent (N-75 60% acetic-acid solution of poly isocyanate curing agents made from Sumitomo Bayer Urethane) 10 weight section, and the butyl-acetate 45 section were mixed, and it considered as coating liquid.

[0031]

Example 7 Acrylic resin coating Resin : [AKURIDIKKU A-198XB] The 48.0 sections Photocatalyst : [TIPAQUE STE-01] The 25.05 sections Color pigment : [TIPAQUE CR-97] The 5.45 sections Solvent : [Butyl acetate] The 50.0 sections Additive: DISRER BYK163 The 3.0 sections AKURIDIKKU A-198XB : The Dainippon Ink & Chemicals, Inc. make The raw material mixture of the acrylic resin above was put into the beaker, the glass bead 200 weight section with a particle size of 1.2-1.5mm was supplied to this, the dissolver distributed for about 20 minutes at the rate of 1200rpm, filtration removed the glass bead after distributed termination, and dispersion liquid were obtained. This dispersion-liquid 90 section and the butyl-acetate 45 section were mixed, and it considered as coating liquid.

[0032] About the coating of examples 2-7, the accelerated weathering test and NO decomposition trial were performed like the example 1.

[0033] Creation and a test method of a test piece: The coating of examples 2-7 was applied to the glass plate and the plate painted [fluorine coating enamel] with the spray gun for paint, and examples 2, 4-7 used as the test piece what will be dried at a room temperature for 14 days. The example 3 used as the test piece what carried out printing hardening for 180 degree-Cx 20 minutes after 1-hour setting at the room temperature. About what carried out spreading desiccation among creation test pieces at the plate painted [fluorine coating enamel], it is JIS. Promotion exposure of 1000 hours and 2000 hours is carried out with the sunshine weather meter specified to K5400, and it is JIS about whenever [paint film surface degradation]. Whenever [chalking / which is specified to K5400] estimated. Moreover, about what carried out spreading desiccation, NO cracking severity was measured by the same approach as an example 1 to the glass plate.

[0034]

[Table 3]

表 3

	実施例２	実施例３	実施例４	実施例５	実施例６	実施例７
サンシャインウエザーメーター１０００時間後						
白亜化度	8	8	8	8	8	8
塗膜外観	○	○	○	○	○	○
サンシャインウエザーメーター２０００時間後						
白亜化度	8	8	8	6	6	6
塗膜外観	○	○	○	○	○	○
ブラックライト４８時間照射後						
ＮＯガス分解性能（%）	64.3	68.3	65.1	67.9	70.4	69.5

[0035] It is clear from the upper result by using a pigment titanium dioxide together to a titanium-dioxide photocatalyst

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CLAIMS

[Claim(s)]
[Claim 1] The titanium-dioxide photocatalyst content coating constituent which distributes a porosity silica covering titanium-dioxide photocatalyst and a pigment titanium dioxide to an organic plastic paint vehicle, and becomes so that the content in a dry paint film may become 5 - 70 % of the weight, and 5 - 50 % of the weight, respectively.
[Claim 2] The coating constituent of claim 1 whose contents of said titanium-dioxide photocatalyst and a pigment titanium dioxide are 30 - 60 % of the weight, and 5 - 20 % of the weight, respectively.
[Claim 3] It is the coating constituent of claims 1 or 2 whose titanium-dioxide photocatalysts are anatase molds and whose pigment titanium dioxides are rutile molds.

[Translation done.]